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THERMAL CYCLIC BEHAVIOR
OF TUNGSTEN - URANIUM
DIOXIDE CERMETS CONTAINING
METAL OXIDE ADDITIVES

by Philip D. Takkunen, Richard E. Gluyas, and Michael A. Gedwill

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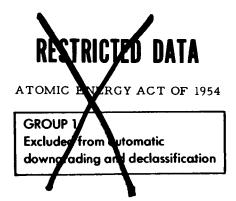
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1967



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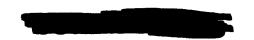
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# THERMAL CYCLIC BEHAVIOR OF TUNGSTEN - URANIUM DIOXIDE CERMETS CONTAINING METAL OXIDE ADDITIVES (U)

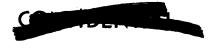
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Lewis Research Center

#### SUMMARY

A major problem encountered in the feasibility study of tungsten-uranium dioxide cermets for the NASA tungsten, water-moderated nuclear rocket concept has been the migration and the subsequent loss of fuel during thermal cycling to temperatures of about 2500° C. Addition of metal oxides to uranium dioxide particles along with complete encapsulation of this cermet with tungsten were the most effective methods found of reducing this fuel migration and loss. In this study of 13 different metal oxides added to uranium dioxide, it was found that cerium oxide and yttrium oxide are two of the more effective additives in reducing fuel loss. Further studies on fully clad cermets containing either cerium oxide or yttrium oxide indicated that while thermal cycling resulted in no observable difference in fuel loss, cerium oxide more effectively inhibited fuel migration through the tungsten matrix. Therefore, cerium oxide appears to be the more promising fuel stabilizer. Additional experiments indicated that increasing the concentration of either cerium oxide or yttrium oxide in uranium dioxide decreased fuel loss and migration.

Examination of the effect of thermal cycling conditions revealed that, after a given number of cycles, increased fuel migration and loss resulted from increasing the peak cycling temperature from  $2500^{\circ}$  to  $2600^{\circ}$  C, increasing the time at peak temperature per cycle from 2 to 120 minutes, and increasing the hydrogen pressure from 15 to 600 psi  $(0.10 \text{ to } 4.1 \text{ MN/m}^2)$ . Increasing the time at peak temperature per cycle also resulted in increased accumulated time at temperature before a particular fuel loss level was reached. In addition, it was observed that dimensional growth was proportional to the number of thermal cycles but appeared to reach a limiting value of about 25 percent after 100 cycles.





One of the major materials problems encountered in a feasibility study of the NASA tungsten, water-moderated nuclear rocket concept (TWMR, ref. 1) was the thermal cyclic-induced migration and subsequent loss of fuel from the tungsten - uranium dioxide (W-UO $_2$ ) cermet fuel element materials. (In this report, fuel is defined as UO $_2$  or UO $_2$  solid solutions with metal oxides.) Development testing and actual operation of nuclear rockets will require the fuel elements to undergo at least 25 thermal cycles between ambient and maximum operating temperatures with less than 1 percent loss of fuel. However, initial tests on W-UO $_2$  cermets under simulated reactor operating conditions (about 2500° C in flowing hydrogen gas) resulted in intolerable fuel losses after only a few thermal cycles (ref. 2). Therefore, this problem has been extensively studied (refs. 2 to 5) to determine the causes and to seek remedies.

These studies indicated that the mechanism by which thermal cyclic-induced fuel migration and losses occur is complex and depends primarily on partial decomposition of  $UO_2$  at high temperatures  $\left(UO_2 - UO_{2-x} + xO\right)$  followed by precipitation of uranium at lower temperatures  $\left(UO_{2-x} - \left(1 - \frac{x}{2}\right)UO_2 + \frac{x}{2}U\right)$ . This resultant free uranium can mi-

grate through the tungsten matrix causing degradation (i.e., loss of strength) and eventual breakup of the cermet to allow extensive volatilization of the remaining fuel. A more extensive discussion of the mechanisms leading to fuel migration and loss is presented in appendix A. The most effective method found to reduce this degradation of W-UO $_2$  cermets was the addition of small amounts of metal oxides, such as calcium oxide (CaO) or yttrium oxide (Y $_2$ O $_3$ ), in solid solution with the UO $_2$  along with complete encapsulation of the cermet with a tungsten cladding. The metal oxide additions were found to "stabilize" (i.e., retard the amount of fuel decomposition) the fuel to the effects of thermal cycling while the cladding prevented vaporization of fuel.

The studies reported herein were a continuation of the previously referenced work. The general objective of this work was to improve further the methods of reducing cermet degradation and fuel losses under thermal cycling conditions. The specific purposes of these studies were (1) to determine the relative effectiveness of 13 selected metal oxides in stabilizing the fuel and (2) to test extensively cermets containing two of the most effective additives (cerium oxide and yttrium oxide) under varying thermal cycling conditions, that is, temperature, time at temperature, and hydrogen pressure.

These objectives were met by fabricating cermets containing 35-volume-percent  $\rm UO_2$  in tungsten by powder metallurgy and hot rolling techniques. These cermets were then thermally cycled under carefully controlled conditions. The results were evaluated on the basis of weight (fuel) loss, dimensional change, radiographic inspection, and metallographic examination.





#### Specimen Preparation

Thirteen metal oxide additives were selected for the initial phase of this study. These oxides (listed in table I) were selected primarily because of their expected solubility with  $UO_2$  (refs. 6 to 9) and their relatively low thermal neutron absorption cross section (required for the TWMR concept). Gadolinium oxide  $(Gd_2O_3)$  has a high cross section, but it was included in the program for comparison purposes because it was reported (ref. 10) to be an effective additive for these cermets. Most of the additive cations selected exhibit only a single oxidation state; however, cerium oxide was added as either  $CeO_2$  or  $Ce_2O_3$  to determine the effect of oxidation state. (See appendix B for the method used to prepare  $Ce_2O_3$  and a discussion of its expected oxidation state in fabricated cermets.)

The solid solutions were prepared by blending, sintering, and crushing fine powders of  $\rm UO_2$  and the desired metal oxide additive as outlined in figure 1. For further details, see reference 3. Chemical analyses of the resulting fuels indicated that the amount of metal oxide additive generally was close to the amount desired (table I). The X-ray diffraction results and reported solubility limits (table I) indicated that at least partial solid solutioning was attained with  $\rm UO_2$  for all additives except titanium oxide ( $\rm TiO_2$ ), and possibly magnesium oxide ( $\rm MgO$ ).

Cermet specimens (25 by 19 by 0.5 mm) containing nominally 35-volume-percent fuel loadings were fabricated according to the procedures summarized in figure 1 and described in detail in reference 11. This fuel loading was chosen to permit comparison with previous studies and because this loading was shown (ref. 4) to be most critical with respect to fuel loss in the range of interest, that is, 10 to 35 volume percent. For ease of preparation, the cermet specimens used for comparison of the 13 metal oxide additives were clad only on the two major surfaces with 0.05-millimeter thick, roll-bonded, tungsten foil (the thin edges were not clad). For all subsequent studies, however, the specimen edges also were tungsten clad but with a relatively thick (6 mm) frame of sintered tungsten powder to reduce the effect of fuel vaporization losses through these edges. The possible effects on fuel losses of the difference in thickness of the edge and face cladding were analyzed and are discussed in appendix C.

All fabricated specimens were radiographically inspected for defects, and only those specimens that were crack-free and highly dense (>98 percent of theoretical density) were evaluated in this study (fig. 2(a)). Furthermore, selected representative specimens were characterized by metallographic examination (fig. 2(b)) and chemical analyses. Typical chemical analyses for cermets without cladding and containing  $\text{Ce}_2\text{O}_3$  or  $\text{Y}_2\text{O}_3$  are listed in table II.





Prior to thermal cyclic testing, all specimens were heat treated in a hydrogen atmosphere: the face-clad specimens were treated at  $2500^{\rm O}$  C to remove  ${\rm UO}_2$  exposed at the edges which were not clad, and the fully clad specimens were treated at  $1650^{\rm O}$  C to remove surface contaminants.

#### Testing Procedure

Most of the thermal cyclic testing was performed in an induction furnace (ref. 12) with 15 psia  $(0.10 \text{ MN/m}^2)$  of hydrogen. However, a few specimens were tested under a higher hydrogen pressure of 600 psia  $(4.1 \text{ MN/m}^2)$  in an all-metal, resistively heated furnace (ref. 13). (The latter testing was done under a NASA contract by R. J. Baker of Battelle Memorial Institute at the AEC's Pacific Northwest Laboratories.) The hydrogen flow in each furnace was about 35 standard cubic feet per hour  $(1.0 \text{ m}^3/\text{hr})$ , and the hydrogen was found to contain less than 10 ppm of water or oxygen impurities. More detailed comparisons of the operating characteristics of these furnaces are described in reference 14.

Each thermal cycle was run as follows:

- (1) Heat up from room temperature to  $2500^{\circ}$  C (or  $2600^{\circ}$  C) in 2 to 3 minutes,
- (2) Hold at 2500° C for 10 minutes (or up to 120 min in some cases), and
- (3) Cool from 2500° C to less than 200° C in about 5 minutes.

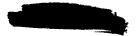
Weights and thicknesses of the thermally cycled specimens were measured periodically (every 5 or 10 cycles), and all weight losses were assumed to result entirely from loss of fuel. Tungsten in the specimens is not believed to have contributed significantly to the weight losses since similar tests on unfueled tungsten blanks revealed no observable weight changes. After completion of testing, all specimens again were radiographed, and selected specimens were metallographically examined.

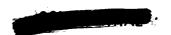
#### RESULTS AND DISCUSSION

### Comparison of Effects of Thirteen Metal Oxide Additives on Fuel Loss

The initial phase of this study was a screening test on the relative effectiveness of 13 selected metal oxide additives in stabilizing W-UO<sub>2</sub> cermets to the degrading effects of thermal cycling. Similarly produced, face-clad cermets containing nominally 10 mole percent of each of the metal oxides listed in table I were thermally cycled to  $2500^{\circ}$  C in hydrogen (for 10 min at  $2500^{\circ}$  C per cycle).

The fuel loss results of tests on the partially clad cermets (fig. 3) suggest that the additives may be separated into four groups of relative effectiveness in reducing fuel





loss; these groups are summarized below:

- (1) Gd<sub>2</sub>O<sub>3</sub>, PrO<sub>2</sub>, and CeO<sub>2</sub> delayed the onset of accelerated fuel loss to the greatest extent.
- (2)  $Yb_2O_3$ ,  $La_2O_3$ ,  $Ho_2O_3$ ,  $Nd_2O_3$ , and  $Y_2O_3$  moderately delayed the onset of accelerated fuel loss.
  - (3) ThO2, SrO, MgO, and CaO slightly delayed the onset of accelerated fuel loss.
- (4)  $TiO_2^-$  had no effect on fuel loss (probably because this oxide does not form a solid solution with  $UO_2$ ).

It is interesting to note that, in general, these results are grouped in accord with the additive cation valence state. The effect of metal oxides on reducing the rate of fuel loss was least for additives with cations having only a +2 or +4 valence (e.g., CaO or  $ThO_2$ ), was somewhat greater for additives having normally only a +3 valence (e.g.,  $Y_2O_3$ ), and was greatest for oxides with cations capable of existing in both +3 and +4 valence states (i.e.,  $CeO_2$ ,  $Ce_2O_3$  and  $PrO_2$ ,  $Pr_2O_3$ ).

 $\mathrm{Gd}_2\mathrm{O}_3$  (cation exhibits only a stable +3 valence) was found to be more effective in reducing fuel loss than the other sesquioxides studied; this is the principal exception to the correlation between additive effectiveness and additive cation valence state. The reason for the superior behavior of  $\mathrm{Gd}_2\mathrm{O}_3$  compared with the behavior of the other sesquioxides is not presently understood. These results, however, are in general agreement with the good cermet stabilizing performance for this oxide reported in reference 10. On the other hand, according to reference 10, cermets containing  $\mathrm{CeO}_2$  did not perform as well as cermets containing  $\mathrm{Gd}_2\mathrm{O}_3$ ; this result is in contradiction to our study. While this contradiction could be due to several factors (e.g., different types of cermets or different test conditions), we believe that the difference may be due to the method of preparing the  $\mathrm{UO}_2\text{-CeO}_2$  solid solution and the resulting oxidation state of cerium in the cermet fuel.

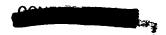
Based on this series of screening tests,  $Y_2O_3$  (which had previously yielded the best stabilizing results, ref. 5),  $CeO_2$ , and  $Ce_2O_3$  were selected for more extensive testing.

#### **Effect of Thermal Cycling Conditions**

Fully clad W-UO $_2$  cermets containing CeO $_2$ , Ce $_2$ O $_3$ , or Y $_2$ O $_3$  in the UO $_2$  were extensively tested to determine the effects on cermet behavior of peak cycling temperature, time at peak temperature per thermal cycle, and hydrogen pressure.

<u>Peak cycling temperature</u>. - Although the TWMR fuel elements would be designed to operate at a maximum temperature of 2500°C, excursions to temperatures of 2600°C or higher may occur. Figure 4 shows the effect of increasing the peak cycling temperature





from  $2500^{\circ}$  to  $2600^{\circ}$  C on fuel loss from cermets. At  $2500^{\circ}$  C, both  $Ce_2O_3$  and  $Y_2O_3$  stabilized cermets performed very well with less than 1-percent loss of fuel after 80 thermal cycles. At  $2600^{\circ}$  C, however, both types of cermets exhibited high rates of fuel loss after only about 30 cycles. Although these cermets met the goal of less than 1-percent fuel loss in 25 thermal cycles, the rapid deterioration of the cermets after 25 cycles to  $2600^{\circ}$  C indicates that temperature excursions exceeding  $2500^{\circ}$  C should be avoided.

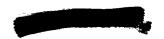
Time at temperature per cycle. - Preflight development testing and actual space flights of nuclear rockets will require the reactor to operate for varying lengths of time. Figures 5(a) and (b) show the effect of the time (2 to 120 min) at temperature per operating cycle on fuel loss from cermets. The results indicate that an increase in the cycle time caused a decrease in the number of cycles that cermets could be operated without excessive fuel losses. However, as shown in figures 5(c) and (d), the total operating time of cermets was increased by increasing the time at temperature. Thus, if a greater number of thermal cycles is desired, the length of each operating cycle can be decreased and vice versa.

Hydrogen pressure. - The tests previously described in this report all were conducted with 15 psia  $(0.10 \text{ MN/m}^2)$  hydrogen pressure for testing convenience. However, fuel elements in nuclear rockets will operate under much higher hydrogen pressures (about 600 psia  $(4.1 \text{ MN/m}^2)$ ). Figure 6 shows the effects of the high hydrogen pressure (600 psia) compared with 15 psia on cermet fuel loss. Under either test pressure, the cermets met the goal of less than 1-percent fuel loss after 25 cycles. However, continued cycling caused the specimens cycled in the high-pressure hydrogen to deteriorate more rapidly than those tested at the low pressure. Although the number of specimens tested in this study was limited, the results are basically in agreement with those reported in reference 14, which indicates that high-pressure hydrogen test conditions are more severe than atmospheric pressure conditions. Reference 10, on the other hand, reports that neither increased hydrogen pressure nor flow rate significantly affects fuel loss. Further work to determine the effects of pressure is needed to resolve these differences.

<u>Cermet specimen growth</u>. - Other investigators (refs. 10 and 15 to 17) have observed appreciable increases in size of W-UO $_2$  cermet specimens after thermal cycling. This growth has been attributed to the thermal expansion mismatch of W and UO $_2$ . (The linear coefficient of thermal expansion of UO $_2$  is about twice that of tungsten.)

In the present investigation, thickness increases were found for all specimens evaluated. A typical example is shown in figure 7. The magnitude of this growth is plotted in figure 8 as a function of the number of thermal cycles to  $2500^{\circ}$  or  $2600^{\circ}$  C. The total growth was found to be a linear function of the number of cycles up to about 100 cycles with a rate of about 0.25-percent growth per cycle. This growth subsided after about





100 cycles with a total thickness increase of about 25 percent. The cessation of growth is probably due to the accommodation of  $\rm UO_2$  expansion as would be expected from the "thermal ratcheting" mechanism proposed in reference 17.

A surprising observation from these results is that the variation in thermal cycling conditions (peak cycling temperatures of 2500° or 2600° C and cycle durations of 2 to 120 min) had no appreciable affect on the growth. This result was unexpected because the growth is thought to result from creep of the tungsten matrix under the thermal strains induced by cycling. Since creep is a function of both temperature and time, the differences in cycling variables should have caused different amounts of growth. The reason for this anomaly is unknown.

The amount of growth illustrated in figure 8 appears intolerable for the use of W-UO $_2$  cermets in nuclear rocket fuel elements because the resulting dimensional changes could greatly alter the flow of the hydrogen propellant. However, results reported in reference 18 indicate that the cermet geometry may control the amount of growth. In that study,  $Y_2O_3$ -stabilized W-UO $_2$  cermets in a hexagonal honeycomb configuration (proposed for the TWMR) exhibited no observable growth after fifty 10-minute thermal cycles at  $2500^{\circ}$  C in hydrogen.

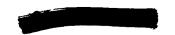
### Comparison of Effectiveness of Cerium Oxide and

#### Yttrium Oxide Fuel Additives

Fuel loss. - Although the results of the screening study on face-clad cermets (fig. 3) indicated that  $CeO_2$  additions to  $UO_2$  were more effective in stabilizing cermets than were  $Y_2O_3$  additions, the results for fully clad specimens containing these additives showed only small differences in effectiveness. For example, no significant differences (at acceptably low fuel-loss levels) were observed when cycling cermets for 10-minute durations to  $2500^{\circ}$  or  $2600^{\circ}$  C (fig. 4). (The effectiveness of  $CeO_2$  and  $Y_2O_3$  should not be compared in fig. 5 because the concentrations of additives in the  $UO_2$  are not equal.)

Fully clad W - 35-volume-percent-UO $_2$  cermets containing different concentrations of  $Y_2O_3$ ,  $CeO_2$ , and  $Ce_2O_3$  in the UO $_2$  were prepared and were thermally cycled (10-min cycles to  $2500^{\circ}$  C in flowing hydrogen) to compare further the effectiveness of these fuel additives and to determine the effect of the valence state of cerium (i.e., +3 and +4). The results, shown in figure 9, indicate that increases in the concentration of any of the three additives improved the fuel retention of cermets subjected to thermal cycling. It also was observed that the onset of rapid fuel loss was about the same for cermets containing additive concentrations which yield approximately the same ratio of oxide cation to uranium. For example, concentrations of 19-mole-percent  $CeO_2$ , 10-mole-percent  $CeO_3$ , and





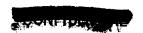
10-mole-percent  $Y_2O_3$  in  $UO_2$  [(Ce/U)  $\approx$  (Y/U)  $\approx$  0.22] all resulted in about 1-percent fuel loss after 80 thermal cycles. These results on fully clad cermets are more meaningful than those on partially clad cermets (fig. 3) because complete cladding will be necessary for fuel elements in a reactor in order to reduce fuel loss to tolerable levels, that is, less than 1 percent.

Fuel migration. - Although the fuel-loss curves showed very little difference in the effectiveness of cerium oxide or yttrium oxide additions, metallographic examination of the cycled cermets indicated that the cerium oxide additives were more effective than yttrium oxide in reducing fuel migration into tungsten grain boundaries. For example, figure 10 shows photomicrographs of thermally cycled cermets which contained  $CeO_2$ ,  $Ce_2O_3$ , or  $Y_2O_3$  additions to the  $UO_2$ . After twenty-five 10-minute cycles to  $2500^{\circ}$  C, the microstructures of all three types of cermet appeared similar to each other and to the typical microstructure of an as-fabricated specimen (fig. 2(b)). After 60 cycles, the cermet containing  $CeO_2$  or  $Ce_2O_3$  showed few signs of degradation, but the cermet containing  $Y_2O_3$  exhibited considerable fuel migration through the tungsten grain boundaries. As discussed in appendix B, no significant differences were found in the behavior of cermets containing  $CeO_2$  or  $Ce_2O_3$  (in the ''as-added'' state) providing the Ce/U ratios were equivalent.

Although fuel migration into grain boundaries did not affect fuel loss from the specimens illustrated in figure 10 (all specimens shown lost less than 1 percent after 60 cycles), this fuel migration can have detrimental effects on cermets. First, the intergranular strength of the tungsten matrix is lowered by the presence of a ceramic phase in the grain boundaries (ref. 19). Second, the thermal expansion mismatch between tungsten and  $\rm UO_2$  would result in a force tending to separate the tungsten grains each time the cermet is heated. Third, fuel may migrate through the cladding of a cermet and thus expose itself to the atmosphere and volatize. The amount of fuel lost through such a cladding flaw will depend upon the extent of fuel-particle interconnection (through matrix grain boundary migration) in the vicinity of the flaw. For these reasons, we believe that  $\rm CeO_2$  and  $\rm Ce_2O_3$  are more attractive than  $\rm Y_2O_3$  for use in a nuclear rocket reactor and that the cerium oxide additives would permit better reliability of the fuel elements.

The mechanisms causing fuel migration in nonstabilized W-UO $_2$  should be known to understand why CeO $_2$  and Ce $_2$ O $_3$  more effectively inhibit fuel migration than Y $_2$ O $_3$  does. A detailed discussion of proposed mechanisms is presented in appendix A. Briefly, fuel migration in nonstabilized cermets is hypothesized to result from decomposition of UO $_2$  (at high temperatures) into oxygen and substoichiometric UO $_2$ . The substoichiometric UO $_2$  disproportionates upon cooling to yield free uranium. The uranium is then free to migrate throughout the tungsten matrix via grain boundaries.

We propose that these additives affect the fuel decomposition but not the disproportionation step. This proposal is based on differential thermal analysis studies of  $UO_2$ 



solid solutions (ref. 20), which indicate that neither cerium oxide nor yttrium oxide have a significant effect on the amount of uranium precipitated out providing the initial oxygento-uranium ratios (before cooling) were equivalent. A decrease in the amount of decomposition of  $\rm UO_2$  by adding metal oxides in solid solution is thought to result from the formation of an oxygen-vacancy-defect crystal structure which exhibits greater thermodynamic stability to loss of oxygen than  $\rm UO_2$  (ref. 3).

The observation that  $Ce_2O_3$  or  $CeO_2$  additives delay migration of  $UO_2$  more effectively than  $Y_2O_3$  may be associated with the existence of a +4 as well as a +3 oxidation state for cerium. It is possible for  $UO_2$  solid solutions containing  $Ce_2O_3$  to hold excess oxygen more firmly than solid solutions containing  $Y_2O_3$  because excess oxygen can be compensated by +4 cerium without formation of less stable +6 uranium as would be required in the  $Y_2O_3$  solid solutions (ref. 21). This excess oxygen may originate during solid solution preparation as discussed in appendix B. As a consequence, the  $Y_2O_3$  solid solution would lose any excess oxygen it might contain more rapidly than a comparable  $Ce_2O_3$  solid solution. This loss would lead to precipitation of uranium on cooling after a lesser number of thermal cycles in  $Y_2O_3$  solid solutions than with  $Ce_2O_3$  solid solutions.

#### SUMMARY OF RESULTS

Based on studies of tungsten - 35-volume-percent-UO<sub>2</sub> cermets stabilized with additives in solid solution with the UO<sub>2</sub> and thermally cycled under a variety of conditions in flowing (35 standard cu ft/hr  $(1.0 \text{ m}^3/\text{hr})$ ), dry hydrogen, the following results were obtained:

1. The addition of 12 metal oxides to  $UO_2$  significantly reduced fuel loss (from cermets clad with tungsten only on their major faces) induced by 10-minute thermal cycles to  $2500^{\circ}$  C in hydrogen at 15 psia (0.10 MN/m<sup>2</sup>). In order of decreasing effectiveness in reducing fuel loss, these additives may be grouped as follows:

Group (1) - 
$$CeO_2(Ce_2O_3)$$
,  $PrO_2(Pr_2O_3)$ , and  $Gd_2O_3$ 

Group (2) - 
$$Y_2O_3$$
,  $Nd_2O_3$ ,  $Ho_2O_3$ ,  $La_2O_3$ , and  $Yb_2O_3$ 

Group (3) - CaO, MgO, SrO, and 
$$ThO_2$$

- 2. Fully clad cermets containing 19-mole-percent  $\mathrm{CeO}_2$ , 10-mole-percent  $\mathrm{Ce}_2\mathrm{O}_3$ , or 10-mole-percent  $\mathrm{Y}_2\mathrm{O}_3$  in the  $\mathrm{UO}_2$  achieved about eighty 10-minute cycles to 2500° C before losing 1 weight percent of their fuel. The cerium oxides were more effective than yttrium oxide in reducing fuel migration into the tungsten matrix. Decreasing the concentration of either cerium oxide or yttrium oxide hastened the onset of accelerated fuel loss from cermets subjected to thermal cycling.
- 3. Increasing the peak cycling temperature from 2500° to 2600° C resulted in a substantial reduction in the number of cycles attained before accelerated fuel loss from fully





clad cermets began. Fully clad cermets containing either  $\mathrm{Ce_2O_3}$  or  $\mathrm{Y_2O_3}$ , however, still achieved more than 30 cycles to  $2600^{0}$  C before losing 1 weight percent of their fuel.

- 4. Increasing the time at temperature per cycle from 2 to 120 minutes resulted in a reduced number of cycles but an increased total time at temperature before an equal amount of fuel was lost from fully clad cermets containing CeO<sub>2</sub> or Y<sub>2</sub>O<sub>3</sub>.
- 5. Increasing hydrogen pressure from 15 to 600 psia (0.10 to 4.1  $MN/m^2$ ) hastened the onset of accelerated fuel loss from fully clad cermets containing  $Ce_2O_3$ . However, the cermets cycled in high pressure still attained over 40 thermal cycles before losing 1 weight percent of their fuel.
- 6. Cermet dimensional growth linearly increased with the number of thermal cycles at a rate of about 0.25 percent per cycle up to about 25 cycles. This growth was independent of the other cycling conditions varied in this study, the stabilizing additive used, or the degree of fuel migration.

Lewis Research Center,

National Aeronautics and Space Administration, Cleveland, Ohio, April 13, 1967, 122-28-01-01-22.



# MECHANISMS LEADING TO FUEL LOSS IN W-UO2 CERMETS

#### SUBJECTED TO THERMAL CYCLING

The two major consequences of thermal cycling of cermets consisting of  $UO_2$  particles dispersed in a tungsten matrix are the appearance of a uranium-rich phase (identical in appearance to  $UO_2$ ) along tungsten grain boundaries and the subsequent loss of uranium-bearing material from the cermet (ref. 2). The mechanism by which this redistribution and loss of fuel occurs is complex and is not completely understood, but we believe that it depends primarily on two reactions (refs. 3 and 5). At high temperature (e.g.,  $2500^{\circ}$  C), decomposition of  $UO_2$  occurs according to the following equation:

$$UO_2 \rightarrow UO_{2-x} + x(O)$$
 (O < x < ~0.4)

After decomposition occurs, free uranium segregates from the  $UO_{2-x}$  upon cooling (see ref. 22 for a U -  $UO_2$  phase diagram) according to the following equation, which represents the disporportionation of substoichiometric  $UO_2$ :

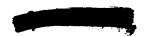
$$UO_{2-x} \to \left(1 - \frac{x}{2}\right)UO_2 + \frac{x}{2}U$$
 (2)

The uranium, which is molten at temperatures above 1130°C, can then wet and dissolve tungsten (ref. 23) and migrate into the tungsten grain boundaries.

The extent to which decomposition proceeds during one thermal cycle depends on the rate of loss of oxygen-rich products through the tungsten matrix and the tungsten cladding. This rate, in turn, depends on the temperature, the time at temperature, the difference between the partial pressures of oxygen over the UO<sub>2</sub> and in the external atmosphere, and the effective thickness of the tungsten cladding (ref. 24). The extent to which decomposition proceeds determines the amount of uranium that forms during the disporportionation which occurs during cooling. This uranium is then free to migrate throughout the tungsten matrix and eventually be exposed to the external atmosphere and volatize. Thus, a higher hydrogen pressure would be expected to increase decomposition and thereby increase fuel loss, as was observed in the present study.

On the basis of the discussion so far, cycled W-UO<sub>2</sub> cermets would be expected to exhibit free uranium or a uranium-tungsten alloy (if the cermet is cooled rapidly enough) in the tungsten grain boundaries. Such a phase has been only rarely observed in W-UO<sub>2</sub> cermets (refs. 2 and 4), and, even in those few cases, the amount of uranium-rich phase





observed appeared to be too low to account for the redistribution of  $\rm UO_2$  in the tungsten matrix. In the present study, uranium or uranium-tungsten phases were not observed in any of the cycled cermets.

We propose that the events leading to the redistribution of  $\rm UO_2$  during thermal cycling are stepwise and as follows: During the hold at maximum temperature in any thermal cycle after the first one, oxygen resulting from decomposition of the  $\rm UO_2$  will permeate into the tungsten and will react with the migrated uranium (formed in the previous cycle) to form  $\rm UO_{2-x}$ . By this stepwise process, a considerable amount of uranium and oxygen can be redistributed in the tungsten and subsequently form  $\rm UO_2$  while little free uranium is present in the tungsten at any one time. Thus, the amount of uranium present in specimens examined may be too fine to be detected at ordinary magnifications. Alternatively, the uranium may alloy with the tungsten and be metallographically indistinguishable from the tungsten matrix.

The redistribution of  $\rm UO_2$  also may be accelerated by other mechanisms. For example, if the uranium which migrates into tungsten grain boundaries is oxidized to  $\rm UO_2$  or hydrided to  $\rm UH_3$  during cooling, the accompanying volume expansion will tend to separate tungsten grains. ( $\rm UH_3$  was not observed in cermets probably because the cooling rate was too rapid to allow much  $\rm UH_3$  formation; therefore,  $\rm UH_3$  is not thought to have a significant effect.) The grains also may be separated by the extrusion of  $\rm UO_2$  which results from the difference in thermal expansion between  $\rm UO_2$  and tungsten. After the tungsten grains have been separated, redistribution of  $\rm UO_2$  may occur by vaporization and condensation of  $\rm UO_2$  into the grain boundaries.





#### APPENDIX B

# PREPARATION OF CERMETS CONTAINING Ce<sub>2</sub>O<sub>3</sub> AND CeO<sub>2</sub>

Preparation of  $\operatorname{Ce_2O_3}$  by hydrogen reduction of  $\operatorname{CeO_2}$  is discussed in reference 25. Several investigators were unable to prepare stable  $\operatorname{Ce_2O_3}$ , and others reported that a pyrophoric substance was produced. Other investigators, however, reported that  $\operatorname{CeO_2}$  could be reduced to a number of intermediate compounds until  $\operatorname{Ce_2O_3}$  was obtained. The color successively changed from a yellowish-white for  $\operatorname{CeO_2}$  to blue-black for the intermediate compounds to yellow-olive for  $\operatorname{Ce_2O_3}$ .

In this study, a 25-gram sample of high-purity  $\text{CeO}_2$  was heated under flowing hydrogen for 6 hours at  $1500^{\text{O}}$  C. The resulting product was yellow-olive in color indicating that  $\text{Ce}_2\text{O}_3$  was formed. This material gained no weight upon exposure to air for 14 days, which indicates that it was stable to oxidation in air at room temperature. Results from X-ray diffraction powder patterns revealed a hexagonal structure with lattice constants of  $a_h = 3.89$  Å and  $C_h = 6.05$  Å. These results compare with values of  $a_h = 3.88$  Å and  $C_h = 6.06$  Å for  $\text{Ce}_2\text{O}_3$  and with  $a_0 = 5.415$  for the  $\text{CeO}_2$  fluorite (FCC) lattice (ref. 25).

An attempt to reduce a larger sample (50 g) of  $\mathrm{CeO}_2$  under the same thermal conditions resulted in the formation of a black substance which was pyrophoric. When the same size sample was thermally treated for a longer time (8 hr), however, complete reduction to the stable, yellow-olive  $\mathrm{Ce}_2\mathrm{O}_3$  was achieved. Therefore, we believe that the partially reduced  $\mathrm{CeO}_x$  (1.5 < x < 2.0) compounds are unstable in air and that complete reduction to  $\mathrm{Ce}_2\mathrm{O}_3$  is necessary to obtain a stable reduced state.

While cerium was added to  $UO_2$  in the form of either  $CeO_2$  or  $Ce_2O_3$ , its oxidation state in a fabricated cermet was not known. It is likely that during solid solution preparation of  $UO_2 \cdot Ce_2O_3$ , some  $Ce^{+3}$  was oxidized to  $Ce^{+4}$  because of the excess oxygen in the ceramic grade  $UO_2(O/U=2.2)$ . During further processing, however, solid solutions containing  $Ce^{+4}$  may have become reduced somewhat because of the thermal treatments in hydrogen (fig. 1). Regardless of whether  $CeO_2$  or  $Ce_2O_3$  was added to the  $UO_2$ , no difference was observed in the behavior of cermets containing these additives. Therefore, the final as-fabricated oxidation state of solid solutions containing either of these additives is believed to be the same.



#### APPENDIX C

# EFFECT OF THICK TUNGSTEN EDGE CLADDINGS ON THERMAL CYCLIC BEHAVIOR OF W-UO<sub>2</sub> CERMETS

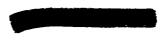
Tungsten-UO<sub>2</sub> cermets for the present study were completely encapsuled by placing tungsten powder along the edges of each cermet plate in a picture-frame arrangement before pressing, sintering, and rolling of the plate. This process resulted in an edge cladding of considerably greater thickness than that expected to be used on actual TWMR fuel elements. Because of this difference, a study was undertaken to determine the effect of the wide edge cladding on thermal cyclic induced fuel loss.

For this study, several cermet plates were prepared with a thick picture-frame-type edge cladding. After the edge claddings of half these specimens were removed, all the specimens were clad by a tungsten vapor deposition process (hydrogen reduction of WCl<sub>6</sub>) to obtain a thin (25 to 50  $\mu$ m) tungsten cladding on all surfaces for comparison of fully clad specimens with and without a wide edge cladding. The results, shown in figure 11, indicate that the wide edge cladding had no significant effect on the average thermal cyclic induced fuel loss. However, it should be pointed out that a wide scatter in results occurred because of the frequent presence of flaws in the vapor deposited coating. These flaws resulted in greater rates of fuel loss than expected for cermets containing cerium oxide either with or without the wide edge cladding. (Compare fig. 9 with fig. 11.)

Figure 12(a) illustrates that fuel loss was more predominant along the interface between the cermet and the wide edge cladding than in other areas of the specimen. Specimens without the wide edge cladding exhibited fuel loss areas which were scattered across the specimen. The preferential loss along the interface is probably due to the difference in thermal cyclic induced volume expansion between the cermet and the wide tungsten edge. We believe the difference in expansion results in stretching of the thinner face cladding along the interface (as was shown in fig. 7) to promote and to accentuate cladding flaws in this vicinity.

Thus, while no conclusive data exist with respect to the effect of the wide edge cladding, we believe that the wide cladding, at best, has no effect on fuel loss or, at worst, reduces fuel retention. The fuel loss results presented in this study, therefore, are thought to be conservative with respect to extrapolation of results to cermets with thin edge claddings.





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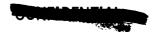




TABLE I. - PROPERTIES OF BINARY OXIDE SYSTEMS OF URANIUM USED IN THIS STUDY

				<del>,</del>	
Valence	Metal	Nominal	Analyzed	$UO_2-M_xO_x$	Reported
group of	oxide	addition	addition	fluorite	solubility
metal	added	to UO2,	to UO2,	unit cell	limits in
oxide	to UO2	mole	mole	dimension, a	υo <sub>2</sub> ,
	_	percent	percent	0 <b>A</b>	mole
					percent <sup>b</sup>
п	MgO	10	15.6	<sup>c</sup> 5.452	d <sub>0 to 25</sub>
	CaO	10	11.3	5.452	0 to 25
	SrO	10	9.9	5.469	0 to 25
III	Y <sub>2</sub> O <sub>3</sub>	10	10.3	5.431	0 to 78
		7.5	7.8	5.438	0 to 78
		5	5.4	5.445	0 to 78
	La <sub>2</sub> O <sub>3</sub>	10	10.2	(e)	<sup>f</sup> 0 to 75
	$Nd_2O_3$	10	10. <b>2</b>	5.459	0 to 64
	$Gd_2O_3$	10	10.1	(e)	<sup>g</sup> 0 to 100
	Ho2O3	10	10.1	(e)	
	Yb <sub>2</sub> O <sub>3</sub>	10	10.4	(e)	
III and	Ce <sub>2</sub> O <sub>3</sub>	10	11.1	5.459	(e)
IV		5	4.9	(e)	(e)
	CeO2	19	20.8	5.461	0 to 100
	_	10	11.1	5.465	0 to 100
		5	5.1	5.469	0 to 100
	PrO <sub>2</sub>	10	(e)	(e)	
IV	TiO <sub>2</sub>	10	(e)	(e)	0
	$ThO_2$	10	10.0	5.482	0 to 100

 $<sup>^{</sup>a}$ Fluorite unit cell dimension of  $UO_{2}$ , 5.471 Å.  $^{b}$ Refs. 6 and 7.

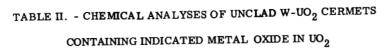
<sup>&</sup>lt;sup>c</sup>Other weak lines were also observed in powder pattern.

d<sub>Providing</sub> excess oxygen is available.

e<sub>Not determined.</sub>

fRef. 8.

gRef. 9.



Metal oxide added to UO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>			
Metal oxide in UO <sub>2</sub> , mole percent	10.3	10.6			
UO <sub>2</sub> in cermet, volume percent <sup>a</sup>	32.6	31.5			
Impurity elements in UO <sub>2</sub> -metal oxide solution, ppm by weight					
	de Bores, Fr				
Nonmetallic	30	30			
As —	<1	<1			
В	40	22			
C Clp	70	8			
	5	31			
F	6	10			
N	<50	<50			
P	<1	<1			
S	2	<1			
Si	-	<u> </u>			
Metallic		<1			
Ag	<1	5			
<b>A</b> 1	5	<1			
Au	<1	<10			
Ва	<10	<1			
Ве	<1	<1			
Bi	<1	<0.2			
Cd	<0.2	<1			
Со	<1	10			
Cr	20	<1			
Cu	1	30			
Fe	60	<1			
Ga	<1	<1			
Hf	<1	<1			
Hg	<1	<3			
In	<3	5			
Mg	10	1			
Mn	5	7			
Мо	<1	<1			
Nb	5	5			
Ni Di	<3	<3			
Pb	<1	<1			
Sb	1	<1			
Sn	6	5			
Ta	2	2			
Ti	<2	<2			
T1 V	<1	<1			
ı V	<1				
Zn	<20	<20			

<sup>&</sup>lt;sup>a</sup>Volume percents were converted from weight percents assuming theoretical densities.

b<sub>Halogens</sub> other than fluorine reported as chlorine.



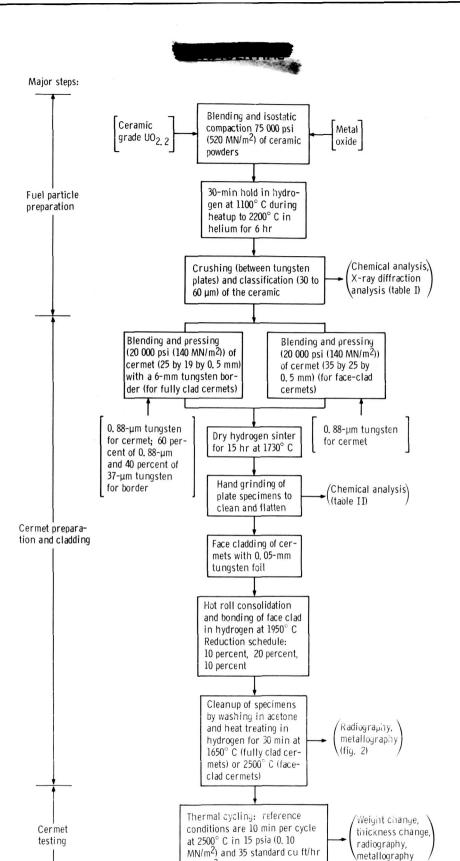
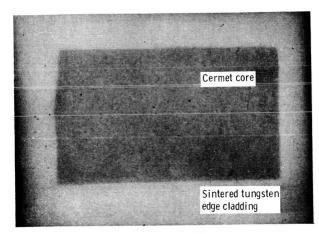


Figure 1. - Preparation and testing of cermet specimens.

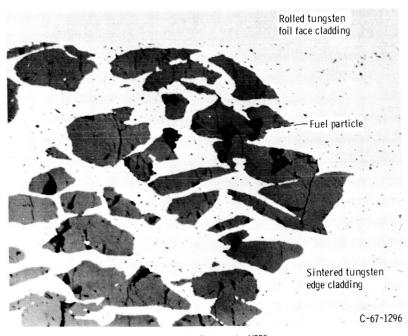
(1.0 m<sup>3</sup>/hr) hydrogen





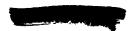


(a) Radiograph; X2.



(b) Photomicrograph; X250.

Figure 2. - As fabricated fully clad tungsten - 35 volume-percent-UO  $_{\rm 2}$  cermet.



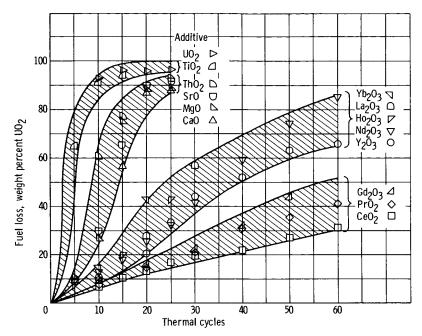


Figure 3. - Effect of metal oxide additions to UO<sub>2</sub> on thermal cyclic induced fuel loss from face-clad tungsten - 35-volume-percent UO<sub>2</sub> cermets (nominally 10 mole percent of metal oxide in UO<sub>2</sub>). 10-Minute cycles to  $2500^{\circ}$  C in hydrogen at 15 psia (0. 10 MN/m<sup>2</sup>) and 35 standard cubic feet per hour (1.0 m<sup>3</sup>/hr).

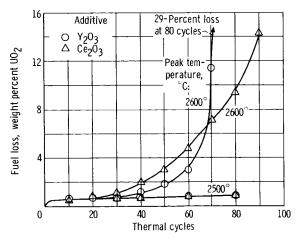


Figure 4. - Effect of peak thermal cycling temperature on fuel loss from fully clad tungsten - 35-volume-percent-UO2 cermets containing 10 mole percent of indicated additive in UO2. 10-Minute cycles to indicated temperature in hydrogen at 15 psia (0, 10 MN/m²) and 35 standard cubic feet per hour (1, 0 m³/hr).





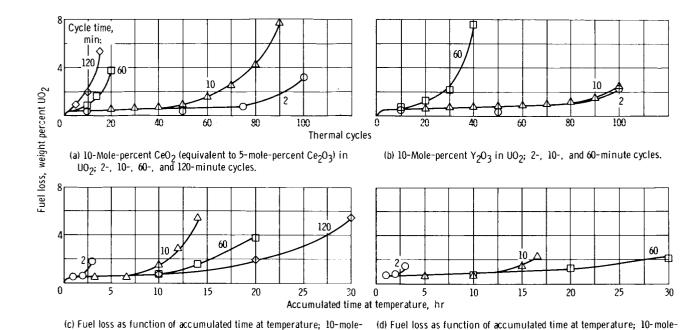


Figure 5. - Effect of time at temperature per thermal cycle on fuel loss from fully clad tungsten - 35-volume-percent-UO2 cermets containing indicated additive. Cycled to 2500° C in hydrogen at 15 psia (0, 10 MN/m²) and 35 standard cubic feet per hour (1, 0 m³/hr).

percent  $Y_2O_3$  in  $UO_2$ ; 2-, 10-, and 60-minute cycles.

percent CeO<sub>2</sub> in UO<sub>2</sub>; 2-, 10-, 60-, and 120-minute cycles.

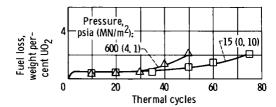
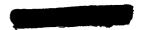
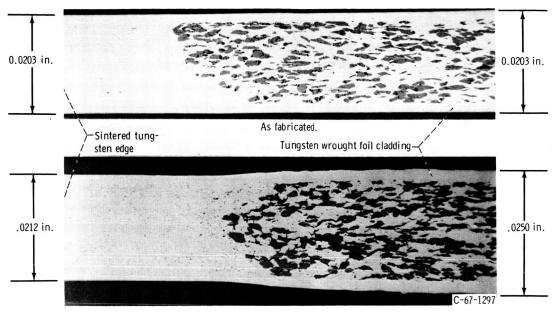


Figure 6. - Effect of hydrogen pressure on thermal cyclic induced fuel loss from fully clad tungsten - 35-volume-percent UO<sub>2</sub> cermets containing 10-mole-percent Ce<sub>2</sub>O<sub>3</sub> in UO<sub>2</sub>. 10-Minute cycles to 2500° C in hydrogen at indicated pressure and 35 standard cubic feet per hour (1.0 m<sup>3</sup>/hr). All specimens from common lot and cycled at Battelle Northwest Laboratories. Two specimens were cycled at high pressure, and one specimen at low pressure.







After sixty 10-minute thermal cycles; 17.9-percent increase in thickness; 1.8-weight-percent

Figure 7. - Thermal cyclic induced dimensional growth of fully clad tungsten - 35-volume-percent  $UO_2$  cermets stablized with 10-mole-percent  $Y_2O_3$ . Cycled to  $2500^\circ$  C in dry hydrogen at 15 psia  $(0.10 \text{ MN/m}^2)$  and 35 standard cubic feet per hour  $(1.0 \text{ m}^3/\text{hr})$ .

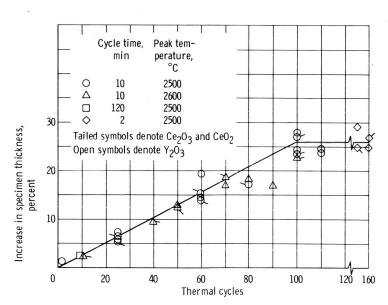


Figure 8. - Thermal cyclic induced dimensional growth of fully clad tungsten - 35-volume-percent-UO $_2$  cermets containing 10-mole-percent Ce $_2$ O $_3$ , CeO $_2$ , or Y $_2$ O $_3$  in UO $_2$ . Cycled to indicated temperature in hydrogen at 15 psia (0. 10 MN/m²) and 35 standard cubic feet per hour (1. 0 m³/hr).





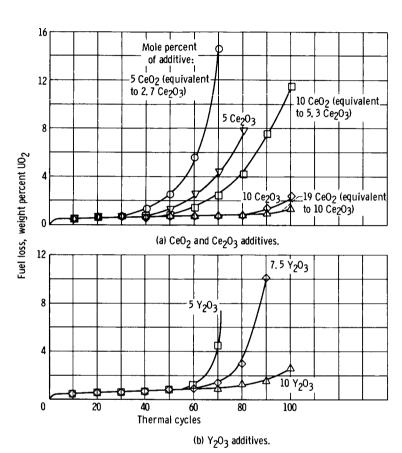


Figure 9. - Effect of additive concentration in  $\rm UO_2$  on thermal cyclic induced fuel loss from fully clad tungsten - 35-volume-percent- $\rm UO_2$  cermets. 10-Minute cycles to 2500° C in hydrogen at 15 psia (0, 10 MN/m²) and 35 standard cubic feet per hour (1, 0 m³/hr).

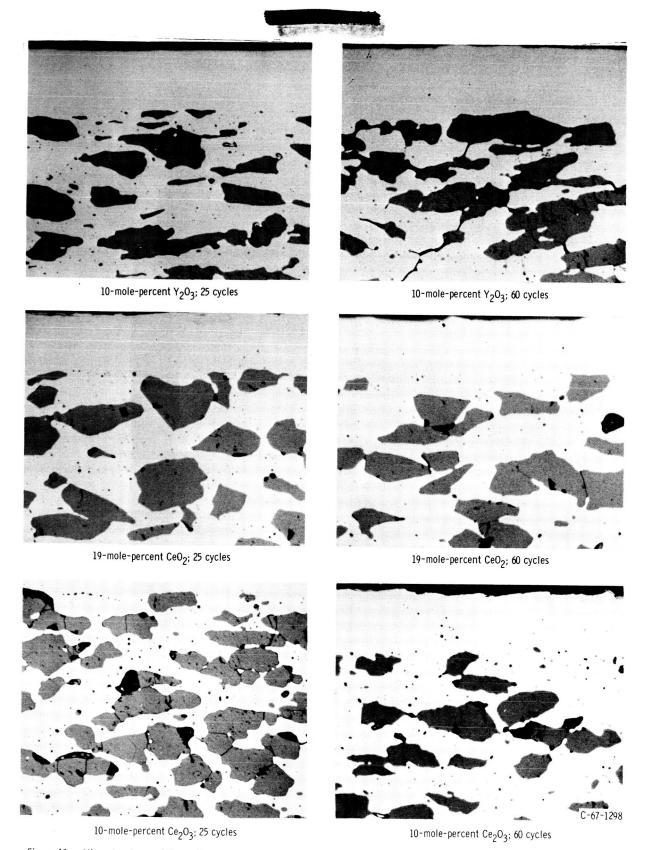
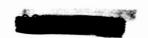


Figure 10. - Microstructures of thermally cycled cermets. Fully clad tungsten - 35-volume-percent-UO $_2$  cermets (containing metal oxide additions to UO $_2$  at indicated concentrations) were cycled to 2500 $^{\circ}$  C for 10 minutes per cycle in hydrogen at 15 psia (0. 10 MN/m $^2$ ) and 35 standard cubic feet per hour (1. 0 m $^3$ /hr). All cermets illustrated lost less than 1-weight-percent fuel. Unetched; X250.



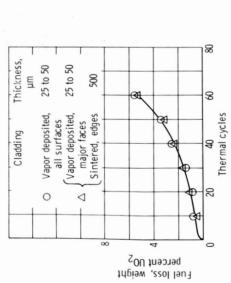
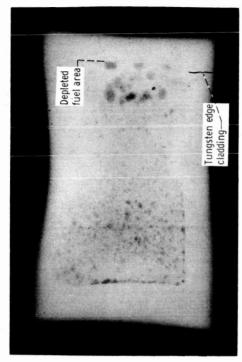
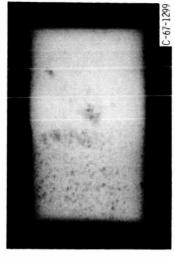


Figure 11. - Effect of a constraining tungsten edge cladding on thermal cyclic induced fuel loss from tungsten - 35-volume-percent-UO<sub>2</sub> cermets which were clad on their surfaces as indicated. 10-Minute cycles to 2500° C in hydrogen at 15 psia (0.10 MN/m<sup>4</sup>) and 35 standard cubic feet per hour (1.0 m<sup>3</sup>/hr).



(a) Wide (500- $\mu$ m) edge cladding, thin (25- to 50- $\mu$ m) face cladding; 5.3-weight-percent fuel loss.



(b) Thin (25- to 50-µm) cladding on all surfaces; 5.8-weight-percent fuel loss.

Figure 12. - Radiographs of thermal cycled cermets containing tungsten - 35-volume-percent  $\mathrm{UO}_2$  and  $\mathrm{10}$ -mole-percent  $\mathrm{Ce_2O_3}$  in the  $\mathrm{UO}_2$ . Sixty  $\mathrm{10}$ -minute cycles to 2500°C in hydrogen at 15 psia (0. 10  $\mathrm{MN/m^2}$ ) and 35 standard cubic feet per hour (1. 0  $\mathrm{m^3/hr}$ ); X2.

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